

SPECTROSCOPIC INVESTIGATION OF THE EFFECT OF MEDIUM ON THE FREQUENCY OF IR RADIATION

M. I. NASSER

Department of Physics, University of Kuwait

AND

A. H. BASSYOUNI

Department of Physics, University of Zagazig, Egypt

Abstract. An extensive spectroscopic study of the solvent effect upon the frequency of IR-absorption bands is presented. Due to the special importance of the (X-H) bonds, this study was restricted to the (N-H) and the (O-H) bonds of diphenylamine and α -naphthol respectively.

The frequency of both the (N-H) and the (O-H) groups in the gas state (ν_g) was experimentally measured using a specially designed heated gas cell. It was found that: ν_g (N-H) = 3436 cm⁻¹ and ν_g (O-H) = 3658 cm⁻¹. Thus the solvent frequency shifts could be precisely determined. The attribution of the frequency shifts to both the solvent dielectric properties and to the solute-solvent interactions is fully investigated. It was found that in the case of the nonpolar solvents, the dielectric properties play the major role in the frequency shifts, while in the case of the polar and the aromatic solvents, the solute-solvent interactions play the major role in the frequency shifts. It was also found that the solute-solvent interactions could result in hydrogen bonding formation.

THEORY

The change in the vibrational frequency of a dipole due to its electrostatic interaction was studied by Kirkwood (1934). The model of a point dipole in a continuous dielectric was used. The relative frequency shift is expressed by the Kirkwood - Baur - Magat equation (KBM):

$$\frac{\Delta \nu}{\nu_g} = C \frac{D - 1}{2D + 1} \quad \dots \quad (1)$$

where:

$$\Delta \nu = \nu_g - \nu_s$$

ν_g = vibrational frequency in the gas phase

ν_s = " " in solution "

D = dielectric constant

C = constant depending on solute model

According to this equation, the plot of

$$\frac{\Delta \nu}{\nu_g} \text{ against } \frac{D - 1}{2D + 1}$$

should give a straight line, passing through the origin. Later, they modified their equation and related the frequency shift $\Delta \nu$ to the refractive index of the solvent as follows:

$$\Delta \nu = C' \frac{n^2 - 1}{2n^2 + 1} \quad \dots \quad (2)$$

where:

n = refractive index of the solvent

C' = constant other than C in equation (1)

Josien and Fuson (1954), during their detailed study of the solvent effects on the (N-H) stretching vibrations of pyrrole, showed that only the frequency shifts in dilute solutions of non-polar solvents fall on the KBM line. In polar solvents, the points are shifted towards higher values of $\Delta \nu$. This shift, produced by the polar and aromatic hydrocarbon solvents, has been attributed to the hydrogen bonding formation. Such interactions were not taken into consideration by the KBM equation.

Bayliss *et al.* (1955) also observed that the KBM equation failed to interpret the solvent-

induced frequency shifts for C-H, C=O & C-C vibrations even in the absence of the chemical interactions between the solute and the solvent.

Ooshika (1954), during his investigation of the effect of solvent upon some organic dyes, found that for the polar solvents, the frequency shifts ($\Delta \nu$) could be given by the expression:

$$\begin{aligned} hC \Delta \nu &= \frac{2(D-1)}{2D+1} \alpha \\ &+ \frac{2(n^2-1)}{2n^2+1} \left(\beta - \frac{\gamma}{\nu_s} \right) \\ &+ \frac{2(D-1)}{2D+1} \delta^2 + \left\{ \frac{(2D+1)(n-n^2)}{(2D+n^2)D} \right\} \epsilon \end{aligned} \quad (3)$$

where :

- h = Planck's constant
- C = velocity of light
- ν = solvent wave-number

α , β , γ , δ and ϵ could be calculated by certain equations. They are solute and solvent-dependent. For the non-polar solvents, the above equation (3) is simplified to take the form:

$$\begin{aligned} - \left\{ \frac{2n^2+1}{2(n^2-1)} \right\} \Delta \nu \\ = a + b + \lambda_s \end{aligned} \quad (4)$$

where a and $b \neq 0$

λ_s = absorption wavelength of solvent

Plotting $- \left\{ \frac{2n^2+1}{2(n^2-1)} \right\} \Delta \nu$ against λ_s

should give a straight line.

Mc Rae (1957) studied solvent frequency shifts in detail and derived the following equation:

$$\Delta \nu = A \frac{n^2-1}{2n^2+1} + B \left\{ \frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right\} \quad (5)$$

which is not applicable to the total frequency shifts caused in part by hydrogen bonding. It might be capable of predicting that part of the shift exclusive of the contribution of the hydrogen bonding.

Benson and Drickamer (1957), and Wiederkehr and Drickamer (1958) studied the stretching vibrations of a variety of bonds, mostly containing hydrogen X-H bonds in condensed

systems. They related the frequency shifts to the first and second derivatives of the interaction energy (E_{int}) as follows:

$$\begin{aligned} \Delta \nu &= \frac{1}{8\pi C^2 M_r \nu} \left[-3 \frac{K_{11}}{K_{10}} \times \frac{\delta E_{int}}{\delta r_1} \right. \\ &\left. + \frac{\delta^2 E_{int}}{\delta r_1^2} \right] \quad (6) \end{aligned}$$

This equation applies only to diatomic molecules, but in polyatomic molecules, the localization of vibrations in particular bonds allows the treatment of these bonds as isolated diatomic molecules. It shows that the spectral shift is a function of the energy derivatives rather than the energies themselves. The interaction energy is a resultant of different energy terms which could be due to : dispersion, dipolar orientation, repulsion and induction. These energy terms could be written as:

$$E_{dis} = - \frac{\alpha_1 \alpha_2}{R_{12}^6} \cdot \frac{I_1 I_2}{I_1 + I_2}$$

$$E_{or} = \frac{\mu_1 \mu_2}{R_{12}^3} \phi$$

$$E_{rep} = a \exp(-b R_{12})$$

$$E_{ind} = \frac{\mu_1^2}{a C^3} \cdot \frac{n^2-1}{2n^2+1}$$

where:

notations 1 and 2 refer to solute and solvent respectively

α 's = bond polarizabilities

I 's = bond ionization energies

R_{12} = effective interbond distance

ϕ = orientation factor

μ = dipole moment

Neglecting the second derivatives in equation (6), it could be seen from equation (7) that the dispersion forces produce red shifts (decrease in frequency) while repulsive forces produce blue shifts (increase in frequency).

Pullin (1958) modified the dielectric theory by assuming that the point poles lie within, but not necessarily at, the center of a spherical cavity in a continuous dielectric. Taking into consideration the changes in equilibrium bond lengths in solution and the electronic and atomic polarizations of the solute molecule, he derived the expression:

$$\frac{\Delta \dot{\nu}}{\dot{\nu}_g} = \frac{1}{K(1-A)} \cdot \frac{3f'_0 b \mu_0 \dot{\mu}'}{1} + \frac{f'_\nu B \mu_0 \dot{\mu}'}{2} + \frac{f''_\nu \dot{\mu}'^2}{2} + \frac{1}{2} (f'_0 + f'_{2\nu}) \mu_0 \dot{\mu}'' \quad \dots (8)$$

where:

K = primary force constant

b = anharmonic potential constant

$f_0, f_\nu, f_{2\nu}$ = functions of the dielectric constant $\frac{2D-2}{(2D+1)a^3}$ at frequencies: zero,

$\dot{\nu}$ and $2\dot{\nu}$ respectively

A & B = constants depending on the electronic polarizability of the solute molecule

$\dot{\mu}'$ and $\dot{\mu}''$ = first and second derivatives of the dipole moment.

The first two terms in equation (8) result from the change in the internuclear distance and may either be positive or negative. The third term depends on the intensity and always causes a lowering of the frequency. The last term may operate either way.

Unfortunately, Pullin's assumptions are applicable only to the polar and nonpolar solutes in nonpolar solvents only. Pullin has justified that at least for the cases he has studied, the frequency shifts in a series of diverse solvents can be represented by a smoothly varying non-linear function of bulk solvent properties.

Buckingham (1958) evaluated the effect of solute-solvent interactions on vibrational spectra, by assuming that the interaction energy 'U' can be expanded as a power series in the normal coordinates of the molecule. By treating 'U' and the anharmonic terms in the potential energy function of the free molecule as small perturbations to the harmonic Hamiltonian oscillator, the solvent shifts have been found to be proportional to $(\dot{U} - 3\dot{U} \cdot A/\dot{\nu}_e)$, where: \dot{U} and \dot{U}' are the first and second derivatives of U with respect to the normal coordinates, and $A/\dot{\nu}_e$ is the anharmonic constant obtainable from the gas phase spectrum. The simplified Buckingham's equation for small shifts in polar solvents is given by:

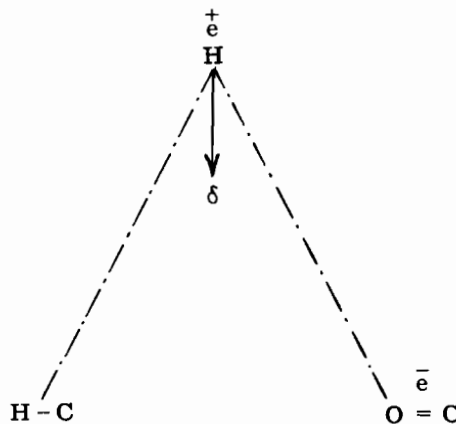
$$\frac{\Delta \dot{\nu}}{\dot{\nu}_g} = C + C_D \frac{D-1}{2D+1} + C_n \frac{n^2-1}{2n^2+1} \quad \dots (9a)$$

For nonpolar solvents, it takes the form:

$$\frac{\Delta \dot{\nu}}{\dot{\nu}_g} = C + \frac{1}{2} (C_D + C_n) \frac{D-1}{D+2} \quad \dots (9b)$$

C, C_D and C_n are constants which may be evaluated by applying equation (9b) to nonpolar solvents yielding C and $(C_D + C_n)$ and then using (9a) to get C_D and C_n in a polar solvent. The theory points out that $\Delta \dot{\nu} / \dot{\nu}_g$ is independent of isotopic substitution as well as the order of transition.

LaLau (1959) observed that the out-of-plane C-H deformation vibrations of aromatic compounds give solvent blue shifts contrary to the predictions of the KBM equations



The localized interaction has been taken into consideration; a semi-quantitative relationship has been developed by picturing the aromatic hydrocarbon in a polar solvent such as a ketone as in the illustration above.

δ = deviation of the H- atom from its equilibrium position

e^+ and e^{-} = excess charges at the H- and O- atoms

F_δ = component of Coulomb attraction acting along H

$$F_\delta = \frac{e^+ \cdot e^-}{r^2} \cdot \frac{\delta}{r} = K' \cdot \delta$$

K' = force constant = $(e^+ \cdot e^-) / r^3$

By substituting $(K + K')$ for K in the frequency relation: $4\pi^2 \hat{\nu}^2 = K/\mu$ where $\mu =$ reduced mass

The relative frequency will be given by:

$$\frac{\Delta\hat{\nu}}{\hat{\nu}_g} = K' / 2K \quad \dots (10)$$

The order of magnitude of K' in the Coulomb approximation has been estimated for the moments and internuclear distances of the C - H, C = O and CN bonds and the effective arom.

atomic radii of H_2 , O_2 and N_2 .

The $\frac{\Delta\hat{\nu}}{\hat{\nu}_g}$ values thus calculated, show fair agreement with the observed data in the case of benzene in acetone and acetonitrile.

Bellamy *et al.* (1958) have extensively investigated the solvent effects on a number of chromophores of the types X-H and Cy = O, where: X = C, N, O, ... and y = S, C, N, P ... and have successfully supported the local association theory of solute-solvent interactions. A plot of $\Delta\hat{\nu}/\hat{\nu}_g$ for the N-H stretching frequency of pyrrole against $\Delta\hat{\nu}/\hat{\nu}_g$ of X-H in different solvents is found to be linear.

If the dielectric constant alone were important in determining the solvent shifts, the linear plot should have had a slope of unity. But the observed slopes vary widely indicating that the properties of the solute are also involved. Generally, it has been noticed that the solvents which produce large shifts in the case of X-H dipoles do not affect the X=O chromophores greatly and vice versa. The magnitude of the frequency shifts, obviously depends on the proton-donating and the proton-accepting powers of the groups involved and thus simple dielectric effects would not be sufficient to explain the results. Bellamy *et al.* (1958) concluded that "the solvent shifts in all the vibrational transitions are due only to local associations. Such associations occur both in polar and nonpolar solvents, although the association energies may vary widely".

The natural development of the problem is to involve both the electrostatic and local association theories. It has been found possible to relate the observed shifts with quantitative measures of the electron density at the likely centres of interactions (e.g. π - cloud in aromatic systems and C-Cl in halogenated compounds) based upon Taft's inductive and resonance parameters of groups or upon quadrupole coupling constant data.

Caldow and Thompson (1960 a and b) extended the theory to cases dependent on specific interactions. The contribution of the dielectric factors are found to be up to 30% in the case of C=O chromophores. They predicted the addition of an empirical term $C_4\delta$ to Buckingham simplified equations (9 a and b). The values of δ included both the resonance and induction terms ($\delta_I + \delta_R$) in the case of aromatic compounds and only the inductive parameter δ^* in the case of aliphatic derivatives. The two Buckingham equations in their new modified forms became:

$$\frac{\Delta\hat{\nu}}{\hat{\nu}_g} = C_1 + C_2 \frac{D-1}{2D+1} + C_3 \frac{n^2-1}{2n^2+1} + C_4\delta^* \quad \dots (11a)$$

for polar solvents, and

$$\frac{\Delta\hat{\nu}}{\hat{\nu}_g} = C_1 + \frac{1}{2} C_2 \frac{D-1}{2D+1} + \frac{1}{2} C_3 \frac{n^2-1}{2n^2+1} + C_4\delta^* \quad \dots (11b)$$

for nonpolar solvents.

Using the results of some workers (Bellamy *et al.* 1958) which deal with some carbonyl compounds (substituted amides and acetone), the values of the constants C_1, C_2, C_3 and C_4 for the C = O chromophore were calculated. The solvents used for this calculation were selected on the basis that a reliable value of δ^* is known. Thus the contributions to $\Delta\hat{\nu}$, corresponding to each of the four terms in the expression for $\Delta\hat{\nu}/\hat{\nu}_g$, were then calculated. In addition, the coefficients C_1, C_2, C_3 and C_4 were used to predict shifts in other solvents. Check measurements were made. There is excellent agreement between calculated and observed frequency shifts. In all cases, owing to the equivalence of all hydrogen atoms in the solvent, only one method of interaction is effectively possible. In other cases, when two alternative points of attachment are possible, two estimates are calculated for $\Delta\hat{\nu}$, one of which is usually close to that found. Special factors such as shape and size of solvent molecule may also determine which alternative arises in practice. A measure of the bulk dielectric effects is obtained from the sum of the frequency shifts produced from the terms involving C_2 and C_3 expressed as fractions of the whole frequency shifts. In the same manner, the specific local associations can be obtained from the term involving C_4 expressed as a fraction of the whole

frequency shift. The vibrational chromophores used are not diatomic molecules and so it would be unwise to apply the modified Buckingham equations too rigidly. It is unlikely however that the "mass" effects can seriously affect the main conclusions reached. Thus it could be said that neither the dielectric nor the local association factors could be ignored. The relative significance of these two varies from case to case, being dependent on both the chromophores and solvent media.

Ito *et al.* (1959 and 1961) noted that the solvent blue shifts of the $n \rightarrow \pi^*$ transitions of some carbonyl compounds bear a linear relationship to the IR-solvent shifts. He found that the simplified McRae equation (5) also holds for the IR-solvent shifts in both polar and nonpolar solvents in the absence of the hydrogen bonding. It is interesting to be able to compare the solvent effects on the IR-frequencies with those on the electronic spectra.

Hallam (1961), and Hallam and Ray (1961) have recently reviewed the solvent effects on X-H, y=O & C-halogen frequencies and have discussed the relative importance of dipolar interactions and dielectric constant.

Whetsel and Kagarise (1962), during their work on the C=O group found that the solvent frequency shifts do not obey the KBM relationship (equation 1). They also found that Buckingham's relationships (9a and 9b) do not hold. They explained this disagreement by assuming that the C-term in equation (9) is not constant. They made a wide investigation on other bonds e.g. O-H of alcohols and generally concluded that theories based solely on bulk dielectric considerations do not explain the observed shifts. It is suggested that non-dipolar interactions, such as dispersion forces, may contribute to solvent-induced frequency shifts.

Horrocks and Mann (1963), following the predictions of Benson and Drickamer (1957) and those of Wiederkehr and Drickamer (1958) (equation 7) made a quantitative examination of the different interaction energy terms to the solvent frequency shifts of the N-C bond. Considering that $E_{rep} = a/bR_{12}$ will be constant and could be neglected, the derivatives of the remainder energy terms will be:

$$\frac{\delta E_{or}}{\delta r_1} = - \frac{\mu'_1 \mu_2}{R_{12}^3} \cdot K_{or}$$

$$\frac{E_{ind.}^a}{\delta r_1} = - \frac{\mu_1 \alpha_2}{R_{12}^6} \cdot K \cdot a$$

$$\frac{\delta E_{dis.}}{\delta r_1} = - \frac{\alpha'_1 \alpha_2}{R_{12}^2} \cdot K_{dis.}$$

$$\frac{\delta E_{ind.}^b}{\delta r_1} = - \frac{\alpha'_1 \mu_2}{R_{12}^6} \cdot K \cdot b \quad \dots (12)$$

They found that the frequency shifts caused by the non-polar solvents are mainly due to the dominance of both $E_{dis.}$ and $E_{ind.} \times a$. As the polarity of the solvent increases, the terms E_{or} and $E_{ind.} \times b$ can make contribution. The former causes a shift to higher frequencies and the latter a shift to lower frequencies where μ is negative.

David and Hallam (1967), following Benson and Drickamer (1957) and Wiederkehr and Drickamer (1958), and using Debye molecular theory, derived the equation:

$$\Delta \nu = C_1 + C_2 \frac{D-1}{D+2} + C_3 \frac{n^2-1}{n^2+2} \quad \dots (13)$$

which was found to be applicable for both non-polar and polar solvents. It showed a better fit than Buckingham equations (9a and 9b). Recently, Girin, Bakhshiev and Maksimova (1968) taking into consideration the universal interactions, derived an equation according to which the solvent frequency shifts are determined mostly by the anharmonicity of the potential function of the solute molecule. The derived equation has the form:

$$h. \Delta \nu = -\Delta r \left[\frac{\mu_{oe} \left(\frac{\delta \mu}{\delta r} \right) r_e^o (F_1 + F_2)}{1 - \alpha_{oe} (F_1 + F_2)} + \frac{\delta \alpha}{\delta r} r_e^o F_3 \right] \quad \dots (14)$$

where

$$F_1 = \frac{2}{a^3} \left(\frac{D\nu - 1}{2D\nu + 1} \right)$$

$$F_2 = \frac{2}{a^3} \left(\frac{D-1}{2D+1} \right)$$

and

$$F_3 = \frac{3}{2a^3} \cdot \frac{I_1 I_2}{I_1 + I_2} \left(\frac{n^2 - 1}{n^2 + 2} \right)$$

To determine the value of $\delta r = r_{le} - r_{oe}$, it is necessary to use in the first approximation the anharmonic potential function of the molecule in the gas phase represented as a polynomial in $r - r_e^o$, where:

μ_{oe} = equilibrium dipole moment of the solute molecule in the ground state

α_{oe} = polarisability of the solute molecule in the ground state at equilibrium

a = cavity radius

$D\hat{\nu}$ = dielectric constant of the solvent at frequency $\hat{\nu}$

I = ionization potential of the solvent

n = refractive index of the solvent

r_{oe} & r_{ie} = average interatomic distances of the solute bond in the ground ($\hat{\nu} = 0$) and first excited ($\hat{\nu} = 1$) vibrational states respectively

The authors have applied this equation on the HCl molecule dissolved in carbon tetrachloride. They obtained satisfactory results.

EXPERIMENTAL

1. Relating the Frequency shift to $\hat{\nu}_h$

Since both solutes diphenylamine and α -naphthol are in the solid state under the normal conditions, the frequency shift ($\Delta\hat{\nu}_s$) due to solvent effect will be related to $\hat{\nu}_h$ which is the frequency when the material is dissolved in n-hexane (the most non-polar solvent) to find out the behaviour of $\Delta\hat{\nu}_h$.

These measurements were done in 22 solvents and the relative frequency shifts $\Delta\hat{\nu} / \hat{\nu}_h$ with respect to ($\hat{\nu}_h$), the frequency of (N-H) and (O-H) in n-hexane are tabulated and plotted.

Fig. 1a is a plot of $(D-1) / (2D+1)$ against $(\hat{\nu}_h - \hat{\nu}_s) / \hat{\nu}_h$. The data for the figure are tabulated in Tables 1 and 2. This figure shows the relation between the relative frequency shifts of the stretching vibration of the (N-H) group of diphenylamine and the dielectric properties of each solvent. The graph is a straight line obeying the KBM equation. The representative points of the nonpolar solvents fall on or near the straight line, while those of the polar and aromatic solvents fall far from it.

Fig. 1b is a plot of $\frac{n^2 - 1}{2n^2 + 1}$ against $(\hat{\nu}_h - \hat{\nu}_s) / \hat{\nu}_h$ for each solvent. The data upon which this figure is based are given in Tables 1 and 2. The plot is a straight line and obeys the modified KBM equation. The nonpolar solvents fall on or near the straight line but the polar and aromatic solvents fall far from it.

Figs. 2a and 2b are similar representations as Figs. 1a and 1b but for the relative frequency shifts of the (O-H) group of α -naphthol. They exhibit similar behaviour of the solvent

frequency shifts as in the case of the (N-H) group of diphenylamine.

Fig. 3 is a plot of $(\hat{\nu}_h - \hat{\nu}_s) / \hat{\nu}_h$ for the (N-H) group of diphenylamine against $(\hat{\nu}_h - \hat{\nu}_s) / \hat{\nu}_h$ for the (O-H) group of α -naphthol. The data of this figure is in Table 2. The graph is a straight line passing through the origin. The slope of this line is not equal to unity. This shows that the frequency shift is not only due to the dielectric effects of the solvent but also due to the interactions between the solute and solvent molecules. This result supports Bellamy's postulates of the specific local interaction theory.

2. Relating the Frequency Shifts to $\hat{\nu}_g$

$\hat{\nu}_g$ is the frequency of the solute in the gas state. It is clear from the theory mentioned earlier in this work that $\hat{\nu}_g$ should be known for the study of the solvent effect in a more detailed and precise manner. Relating the frequency shift to $\hat{\nu}_h$ provides a relative study only. It could be noticed from most of the published literature that the substances studied were either gases or liquids of low boiling points for which $\hat{\nu}_g$ could be easily experimentally determined. The constants of Buckingham's equations (9a and 9b) and their modified forms (11a and 11b) suggested by Caldwell, Jones and Thompson (1960) were calculated. So also the constants of Mc Rae's equation. Substituting these values of the constants in their related equations, $\hat{\nu}_g$ value was calculated.

The values of $\hat{\nu}_g$ resulting from Buckingham's form and its modified forms were not convenient.

The values resulting from Mc Rae's form and from the extrapolation methods were similar and could be accepted. They are 3451 cm^{-1} for (N-H) group of diphenylamine and 3682 cm^{-1} for (O-H) of α -naphthol. These values could not yet be completely satisfactory. Some new concepts are presented by the authors and are discussed in some detail later in this work.

A special gas cell was designed by the authors and $\hat{\nu}_g$ was experimentally determined.

The measured values are:

$$\hat{\nu}_g \text{ (N-H) diphenylamine} = 3436 \text{ cm}^{-1}$$

$$\text{and } \hat{\nu}_g \text{ (O-H) } \alpha\text{-naphthol} = 3658^{-1}$$

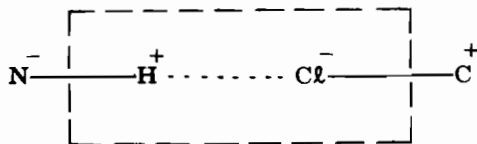
From Tables 1 and 3, plotting $\Delta\hat{\nu} / \hat{\nu}_g$ against $\frac{D-1}{2D+1}$ and $\frac{n^2-1}{2n^2+1}$ of each solvent for both (N-H) and (O-H) groups, Figs. 4a, 4b, 5a and

5b are obtained. These figures show excellent agreement between both KBM lines (part a in the figures) and the modified KBM - lines (part b in the figures). From the figures, it would also be seen that the lines pass through the origin, and that the nonpolar solvents fall on the lines. These figures would enable us to explain the behaviour of solvents in more detail.

The solvents could be arranged in three sets according to their similarity in behaviour and structure:

a. *Aliphatic Nonpolar Solvents:*

These solvents fall on the KBM line which means that the relative frequency shifts are mainly due to their dielectric properties: n. hexane, n. heptane, iso-octane and cyclohexane fall exactly on the line. Carbon-tetrachloride and tetrachloroethylene deviate slightly from the line. This may be due to a sort of interaction resulting from the induced negative charge formed on the Cl - atom



Carbon disulphide (7) which is a nonpolar solvent deviates appreciably from the KBM - line. This may be due to the presence of an excessive negative charge on the C - atom of the CS molecule. Thus, interaction could be effectively present.

b. *Aliphatic Polar Solvents:*

All aliphatic polar solvents (8-15) deviate from both KBM - lines. This deviation could be attributed to the dipole - dipole interaction. The bonds under investigation are also polar bonds:

$$\mu (\text{N - H}) = 1.3 \text{ D/A}$$

$$\mu (\text{O - H}) = 1.43 \text{ D/A}$$

The weaker polar solvents, e.g. 1,2, - dichloroethane (14) ($\mu = 1.19 \text{ D/A}$) fall nearer to the lines than the stronger polar solvents, e.g., acetonitrile (15) ($\mu = 3.84 \text{ D/A}$). That is not always true: ethyl bromide (13) with $\mu = 2.02 \text{ D/A}$ falls nearer to the line than methyl iodide (11) whose $\mu = 1.67 \text{ D/A}$. This means that the interaction does not depend only on the magnitude of the dipole moment but also upon other factors as well.

Diethyl ether (10) is not a strongly polar solvent ($\mu = 1.15 \text{ D/A}$) but it has the greatest

shift. It falls further than the representative points of the other polar solvents. This may be due to the presence of relatively excessive negative charges on the oxygen atom of its molecule which may cause greater interaction.

c. *Aromatic Solvents:*

The aromatic solvents (16-22) may be either nonpolar or polar. Benzene (16), the most prominent member, is a nonpolar solvent ($\mu = 0$) and thus the expected shift is small. But actually it does cause a relatively large frequency shift (about 32 cm^{-1} for N-H and 114 cm^{-1} for O-H (Table 3). This behaviour could be explained if the presence of the π - electron clouds are able to interact with the positive hydrogen atoms of the (N-H) or the (O - H) groups.

From Table 3 and Figs. 3 and 4, if we investigate the behaviour of: benzene (16), chlorobenzene (20) and o - dichlorobenzene (21) in this sequence, it could be seen that the π - electron clouds in the aromatic solvents are more responsible for the frequency shifts than the polar properties. This fact is clear from the following data:

Solvent	$\Delta \tilde{\nu}_s(\text{N-H})$	$\Delta \tilde{\nu}_s(\text{O-H})$	$\mu \text{ D/A}$
Benzene	32 cm^{-1}	114 cm^{-1}	0
Chlorobenzene	24	89	1.67
O. Dichlorobenzene	21	87	2.48

This shows that the shift decreases despite the increase of the dipole moment. Thus it could be concluded that this decrease in $\Delta \tilde{\nu}_s$ is due mainly to the decrease of the π - electron density from benzene to chlorobenzene to o - dichlorobenzene. The Cl-group is an electron attractive group. Thus the presence of one Cl-atom in chlorobenzene lowers the π - electron density than in benzene. The presence of two Cl - atoms in o - dichlorobenzene lowers the density still more than in chlorobenzene. On the other hand, when the π - electron density is elevated, the vibrational frequencies of both the (N - H) and (O - H) bonds shift towards lower values, i.e. $\Delta \tilde{\nu}_s$ increases. This could be done by introducing the aliphatic (-CH) group, which is an electron donating group, in the benzene ring such as toluene (18) and m. xylene (17). From Table 3 it could be noted that:

$$\Delta \tilde{\nu}_s(\text{benzene}) < \Delta \tilde{\nu}_s(\text{toluene}) < \Delta \tilde{\nu}_s(\text{m-xylene}).$$

This might be explained by saying that, as the π -electron density increases, the interaction be-

comes stronger, and hence the frequency shift becomes larger.

Dealing with nitrobenzene (22), its dielectric constant is relatively high ($D = 33.7$), also its dipole moment is relatively high $\mu = 4.27$ D/A. Thus the dielectric shift caused by it, is expected to be relatively high. But it produced shifts similar to those solvents of lower polarity:

$$\Delta\dot{V}_s = 40 \text{ cm}^{-1} \text{ for (N-H)}$$

$$\Delta\dot{V}_s = 168 \text{ cm}^{-1} \text{ for (O-H)}$$

The NO_2 - group is an electron attractive group which causes a decrease in the π - electron density i.e. decreases the frequency shift, but its strong dipolar character must play its role in the interaction which will therefore cause a large frequency shift.

Some authors explain this behaviour of nitrobenzene by assuming that its molecules are in the form of dimers, the active dipoles being buried in the center of the double molecule in such a way as to make it essentially weak polar. But it could be seen from Figs. 4 and 5 that nitrobenzene (22) does not fall near the KBM line which means that it behaves as a polar solvent. This behaviour disapproves with the nonpolar (or weak polar) assumption of the nitrobenzene molecule. From the authors' point of view, nitrobenzene behaves as a polar solvent and interaction is actually present, which appears in a clearer picture during the two component solvent consideration.

Dealing with the aromatic solvents as a whole, another point of interest is relating the frequency shifts to the basicity of the aromatic solvents according to the following data:

Solvent	Henry's Law	$(\Delta\dot{V}/\dot{V}_g) \cdot 10^2$	$(\Delta\dot{V}/\dot{V}_g) \cdot 10^2$
	const. K	(N-H)	(O-H)
Benzene	308	0.9310	3.1160
Toluene	299	1.1060	3.3080
m. Xylene	278	1.1640	3.4450

Henry's constant K is taken as a measure of the basicity of the solvent. From Fig. 6, it could be seen that as the basicity of the solvent decreases, the relative shift increases.

If $(\Delta\dot{V}/\dot{V}_g)$ (O-H) is plotted against $(\Delta\dot{V}/\dot{V}_g)$ (N-H), a straight line passing through the origin as in Fig. 7 is obtained. Its slope is more than unity. This means that the relative frequency shifts of the (O-H) group of α - naphthol are greater than those of the (N-H) group of diphenylamine. This would be explained by the fact that μ (O-H) = 1.34

D/A is greater than μ (N-H) = 1.30 D/A. This will lead to the expectation that the interaction between the (O-H) dipole and the solvent molecules is stronger than between the (N-H) dipole and the solvent molecules.

CONCLUSION

From these considerations it could be concluded that the frequency shifts do not depend upon the solvent properties only, but upon the properties of the solute molecules as well. This finding is in agreement with Bellamy's concepts.

This investigation showed that it was necessary to investigate the nature of the different types of interaction. The authors expected that the temperature effect upon the interaction may serve in understanding its nature and properties. This was studied later and is presented in another paper.

REFERENCES

- Bakhschiev, N.G. & Girin, O.P. 1968. Derivation of their equation taking into consideration the universal intermolecular interactions. *Optics & Spect.* 24 : 377-390.
- Bauer, E. & Magat, M. 1938. Their equation expressing the relative frequency shift of a dipole. *J. Phys. Chem. Radium* 9 : 319-330.
- Bayliss, N.S., Cole, A.E.H. & Little, L.H. 1955. Interpretation of the solvent-induced frequency shifts by the KBM equation. *Australian J. Chem.* 8 : 26-40.
- Bellamy, L. J., Hallam, H. E. & Williams, B. L. 1958. Extensive investigation of the solvent effects on a number of chromophores. *Trans. Farad. Soc.* 54 : 1120-1125.
- Benson, Jr., A.M. & Drickamer, H.G. 1957. Study of the stretching vibrations of a variety of bonds. *J. Chem. Phys.* 2 : 1165-1170.
- Buckingham, A.D. 1958. Evaluation of the effect of solute-solvent interactions on vibrational spectra. *Proc. Roy. Soc.* 248 A : 169-170.
- Caldow, G. L., Jones, D. O. & Thompson, H. W. 1960 a. Extension of electrostatic and local association theory. *Proc. Roy. Soc. (London)* 254 A : 1-16.
- Caldow, G. L., Jones, D. O. & Thompson, H. W. 1960 b. Extension of electrostatic and local association theory. *Proc. Roy. Soc. (London)* 254 A : 17-30.
- David, J.G. & Hallam, H. E. 1967. Derivation of their equation applicable for both polar and nonpolar solvents. *Spectrochim. Acta* 32 A : 593-600.
- Girin, O.P., Bakhschiev, N.G. & Maksimova, O.I. 1968. Derivation of their equation taking into consideration the universal intermolecular interactions. *Optics & Spect.* 25 : 22-30.
- Hadzi, D. 1959. *Hydrogen Bonding*. Pergamon Press.
- Hallam, H. E. 1961. *Spectrovision*. Unicam Inst. Ltd., England.
- Hallam, H.E. & Ray, T.C. 1961. Review of solvent effects on X-H, Y=O & C-halogen frequencies. *Nature* 189 : 915-930.
- Horrocks, Jr., W.D. & Mann, E.H. 1963. Quantitative study of different interaction energy terms. *Spectrochim. Acta* 19 A : 1375-1390.
- Ito, M., Inuzuka, K. & Imanishi, S. 1959. On the solvent

- blue shifts of some carbonyl compounds. J. Am. Chem. Soc. 82 : 1317-1330.
- Ito, M., Inuzuka, K. & Imanishi, S.** 1961. On the solvent blue shifts of some carbonyl compounds. Bull. Chem. Soc. Japan 34 : 467-480.
- Josien, M.L. & Fuson, N.** 1954. Study of solvent effects on the N—H stretching vibrations of pyrrole. J. Chem. Phys. 22 : 1169-1180.
- Josien, M.L., Fuson, N., Powell & Utterback** 1952. Study of solvent effects on the N—H stretching vibrations. J. Chem. Phys. 20 : 145-160.
- Kirkwood, J.G.** 1934. Change of the vibrational frequency of a dipole due to its electrostatic interaction. J. Chem. Phys. 2 : 251-260.
- LaLau, C.** 1959. On the solvent blue shifts given by the out-of-plane C—H deformation vibrations of aromatic compounds. Proc. Conf. Mol. Spect., London, 205-220.
- Mc Rae, E.G.** 1957. Study of solvent frequency shifts in detail and derivation of his equation. J. Phys. Chem. 61 : 562-580.
- Ooshika,** 1954. Investigation of the effect of solvent upon some organic dyes. J. Phys. Soc. Japan 29 : 594-600.
- Pullin, A. D. E.** 1958. Modification of the dielectric theory. Spectrochim. Acta 13 A : 125-135.
- Sidgwick, N.V., Hamson, G.C. & Marsden, R.J.B.** 1934. A Table of Dipole Moments. Trans. Farad. Soc. 30.
- Whetsel, K.B. & Kagarise, R.E.** 1962. Disagreement with Buckingham's relations. Spectrochim. Acta 15 A : 315-341.
- Wiederkehr, R.E. & Drickamer, H.G.** 1958. Study of the stretching vibrations of a variety of bonds. J. Chem. Phys. 28 : 311-320.

(Received 17 December 1972)

TABLE 1. Data on solvents. Dielectric constant (D), refractive index (n).

Nonpolar Solvents						
No.	Solvent	D	$\frac{D-1}{2D+1}$	n	$\frac{n^2-1}{n^2+1}$	$\frac{\mu}{D/A}$
1	n. Hexane	1.880	0.1830	1.3754	0.1864	0
2	n. Heptane	1.924	0.1906	1.3876	0.1908	0
3	Iso-octane	1.948	0.1936	1.3981	0.1945	0
4	Cyclohexane	2.040	0.2050	1.4266	0.2042	0
5	Carbon tetrachloride	2.230	0.2250	1.4630	0.2160	0
6	Tetrachloroethylene	2.290	0.2310	1.5055	1.2289	0
7	Carbon disulphide	2.640	0.2610	1.6276	0.2618	0
Polar Solvents						
8	Bromoform	4.390	0.3466	1.5980	0.2544	0.99
9	Chloroform	4.850	0.3600	1.4457	0.2104	1.02
11	Methyl iodide	4.330	0.3457	1.3497	0.1768	1.15
11	Methyliodide	7.000	0.4000	1.5293	0.2358	1.67
12	Ethyl iodide	7.820	0.4099	1.5133	0.2312	1.90
13	Ethyl bromide	9.390	0.4242	1.4239	0.2033	2.02
14	Dichloroethane	10.000	0.4280	1.4443	0.2100	1.19
15	Acetonitrile	37.500	0.4803	1.3460	0.1756	3.84
Aromatic Solvents						
16	Benezene	2.270	0.2290	1.5017	0.2278	0.00
17	m. Xylene	2.360	0.2370	1.4984	0.2268	0.34
18	Toluene	2.370	0.2390	1.4955	0.2259	0.37
19	Bromobenzene	5.400	0.3729	1.4984	0.2268	1.70
20	Chlorobenzene	5.621	0.4111	1.5251	0.2346	1.67
21	o. Dichlorobenzene	9.930	0.4281	1.5524	0.2423	2.48
22	Nitrobenzene	33.700	0.4780	1.5468	0.2407	4.27

TABLE 2. Relative Frequency Shifts $\frac{\Delta\tilde{\nu}}{\tilde{\nu}_h}$ with respect to ($\tilde{\nu}_h$) the Frequency of (N—H) & (O—H) in n. hexane

No.	Solvent	(N—H) diphenylamine			(O—H) — naphthol		
		$\tilde{\nu}_s$ cm	$\Delta\tilde{\nu}$ cm ⁻¹	$\frac{\Delta\tilde{\nu}}{\tilde{\nu}_h} \times 10^2$	$\tilde{\nu}_s$ cm ⁻¹	$\Delta\tilde{\nu}$ cm ⁻¹	$\frac{\Delta\tilde{\nu}}{\tilde{\nu}_h} \times 10^2$
Nonpolar Solvents							
1	n. Hexane	3432	—	—	3624	—	—
2	n. Heptane	3431.5	0.5	0.0145	3622	2	0.0552
3	Iso-octane	3431	1	0.0290	3620	4	0.1104
4	Cyclohexane	3431	1	0.0290	3616	8	0.2208
5	Carbon tetrachloride	3429	3	0.0875	3602	22	0.6071
6	Tetrachloroethylene	3426	6	0.1750	3600	24	0.6623
7	Carbon disulphide	3517	15	0.4370	3584	40	1.1038
Polar Solvents							
8	Bromoform	3413	19	0.5536	3575	49	1.3520
9	Chloroform	3424	8	0.2330	3593	31	0.8554
10	Ether	3340	92	2.6800	—	—	—
11	Methyl iodide	3394	38	1.1073	3524	100	2.7593
12	Ethyl iodide	3391	41	1.1950	3516	108	2.9801
13	Ethyl bromide	3398	34	0.9910	3528	96	2.6490
14	1, 2-Dichloroethane	3409	23	0.6700	3553	71	1.9592
15	Acetonitrile	3380	52	1.5150	—	—	—
Aromatic Solvents							
16	Benzene	3404	28	0.8160	3544	80	2.2075
17	m. Xylene	3396	36	1.0489	3532	92	2.5386
18	Toluene	3398	34	0.9910	3537	87	2.4007
19	Bromobenzene	3407	25	0.7280	3558	66	1.8210
20	Chlorobenzene	3412	20	0.5827	3572	52	1.4350
21	o. Dichlorobenzene	3415	17	0.4953	3574	50	1.3796
22	Nitrobenzene	3396	36	1.0489	3490	134	3.6976

TABLE 3. Solvent Frequency Shifts Relative to (ν), the Frequency in the Gas Phase for both the (N—H) & (O—H) bonds

$$\nu_g = 3436 \text{ cm}^{-1}$$

$$\nu_g = 3658 \text{ cm}^{-1}$$

No.	Solvent	(N—H) diphenylamine			(O—H)	— naphthol	
		$\nu_s \text{ cm}^{-1}$	$\Delta\nu \text{ cm}^{-1}$	$\frac{\Delta\nu}{\nu_g} \times 10^2$	$\nu_s \text{ cm}^{-1}$	$\Delta\nu \text{ cm}^{-1}$	$\frac{\Delta\nu}{\nu_g} \times 10^2$
Nonpolar Solvents							
1	n. Hexane	3432	4	0.1160	3624	34	0.920
2	n. Heptane	3432	4.5	0.0131	3622	36	0.984
3	Iso-octane	3431	5	0.0146	3620	38	1.039
4	Cyclohexane	3431	5	0.0146	3616	42	1.148
5	Carbon tetrachloride	3429	7	0.0204	3602	56	1.531
6	Tetrachloroethane	3426	10	0.0291	3600	58	1.586
7	Carbon disulphide	3417	19	0.0553	3584	74	2.020
Polar Solvents							
8	Bromoform	3413	23	0.6694	3575	83	2.269
9	Chloroform	3424	12	0.3490	3593	65	1.777
10	Ether	3340	96	2.7989	—	—	—
11	Methyl iodide	3394	42	1.2220	3524	134	3.660
12	Ethyl iodide	3391	45	1.3096	3516	142	3.882
13	Ethyl bromide	3398	38	1.1060	3528	130	3.550
14	1,2 Dichloroethane	3409	27	0.7860	3553	105	2.870
15	Acetonitrile	3380	56	1.6298	—	—	—
Aromatic Solvents							
16	Benzene	3404	32	0.9310	3544	114	3.116
17	m. Xylene	3396	40	1.1641	3532	126	3.445
18	Toluene	3398	38	1.1060	3537	121	3.308
19	Bromobenzene	3407	29	0.8440	3559	100	2.730
20	Chlorobenzene	3412	24	0.6985	3572	86	2.351
21	O. Dichlorobenzene	3415	21	0.6112	3574	84	2.296
22	Nitrobenzene	3396	40	1.1680	3490	168	4.590

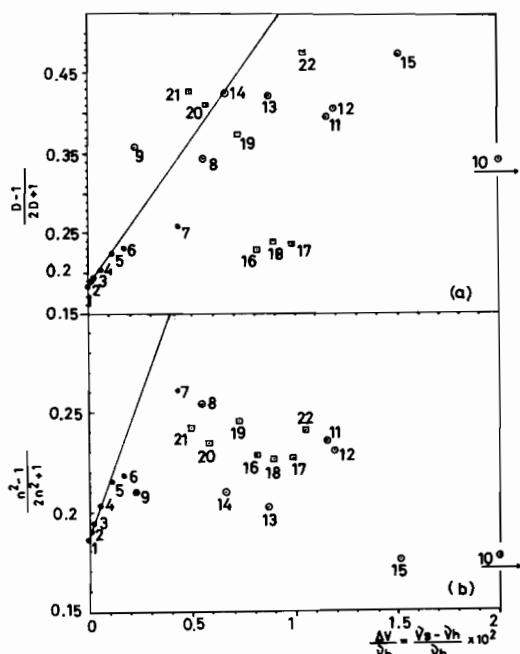


Fig. 1. (N-H) of diphenylamine

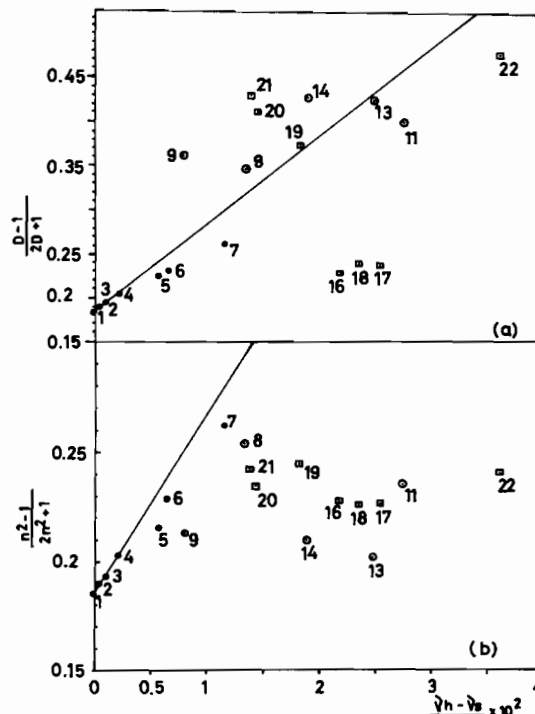


Fig. 2. (O-H) of α -Naphthole

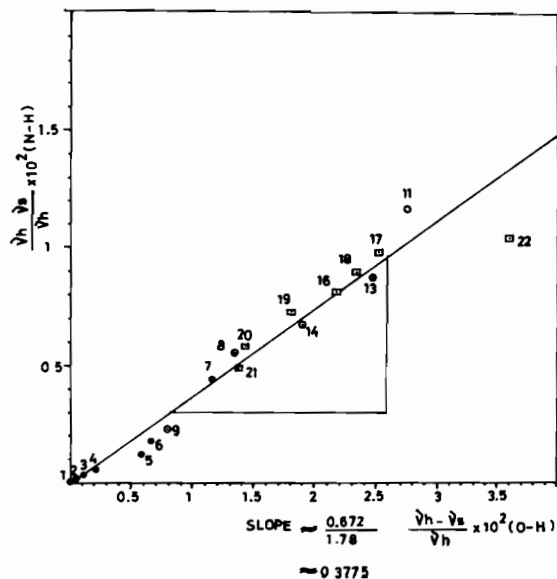


Fig. 3. Relation of $\frac{\nu_h - \nu_s}{\nu_h} \times 10^2$ for the (N-H) bond of diphenylamine Cm against $\frac{\Delta\nu}{\nu_h} - \frac{\nu_s - \nu_h}{\nu_h} \times 10^2$ for the (N-H) bond of diphenylamine α -naphthole.

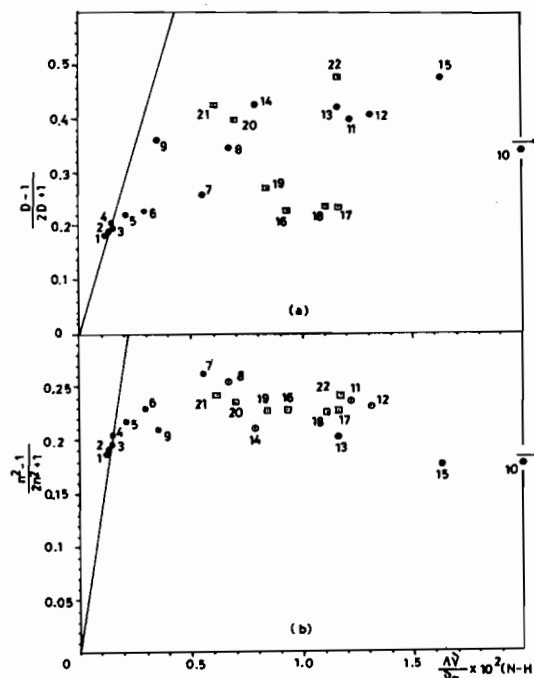


Fig. 4. Relation of $\frac{D-1}{2D+1}$ and $\frac{n^2-1}{2n^2+1}$ against $\frac{\Delta\nu}{\nu_h} - \frac{\nu_s - \nu_h}{\nu_h} \times 10^2$ for the (N-H) bond of diphenylamine.

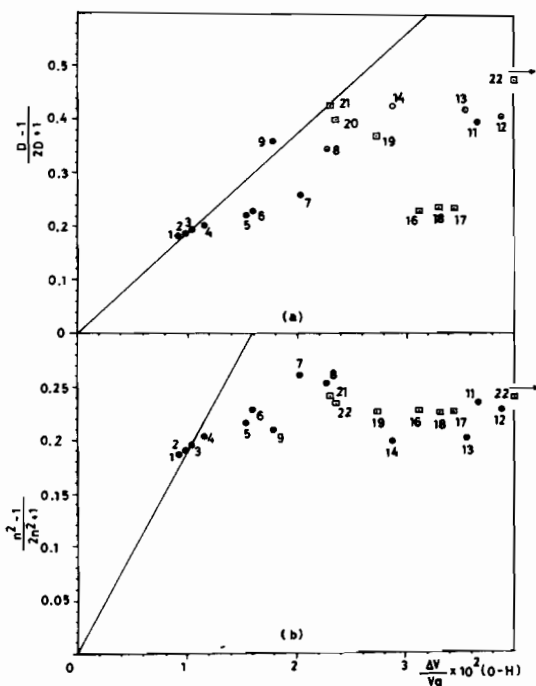


Fig. 5. Relation of $\frac{D-1}{2D+1}$ and $\frac{n^2-1}{2n^2+1}$ against $\frac{\Delta\nu}{V_g} \times 10^2$ for the (O-H) bond of α -naphthol

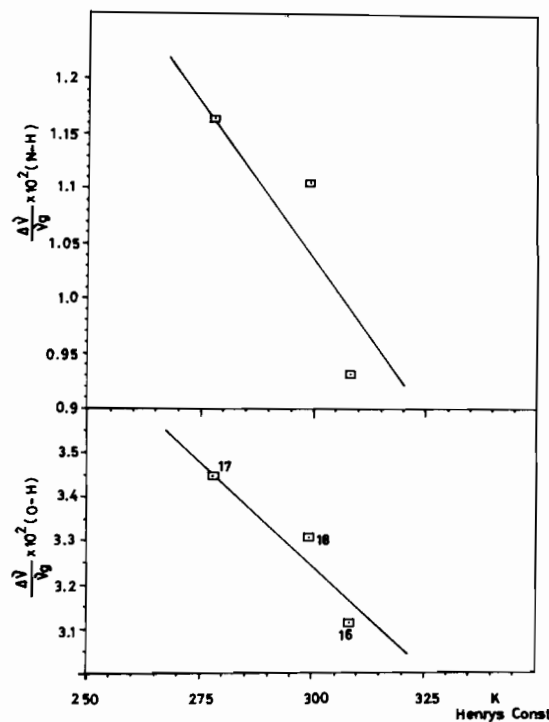


Fig. 6. Relation of $\frac{\Delta\nu}{V_g} \times 10^2$ for both the (N-H) & (O-H) bands against the basicity represented by Henry's Constant K.

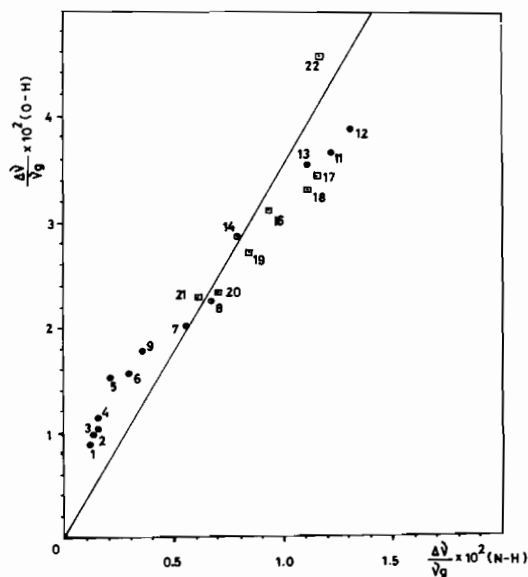


Fig. 7. Relation $\frac{\Delta\nu}{V_g} \times 10^2$ for the (O-H) of α -naphthol against $\frac{\Delta\nu}{V_g} \times 10^2$ for the (N-H) band of diphenylamine.

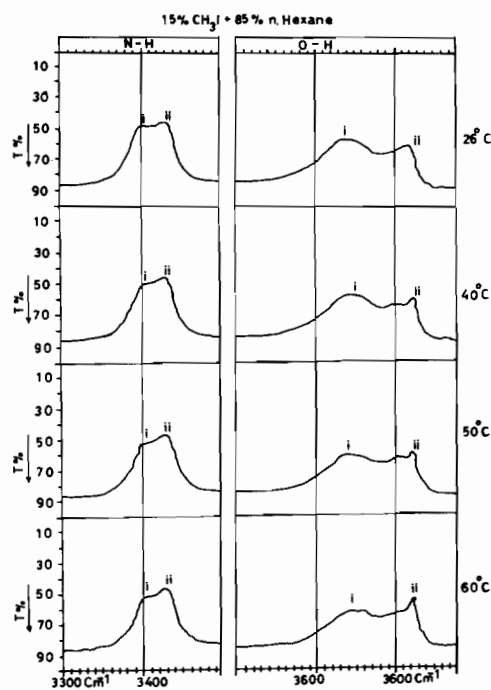


Fig. 8. IR-spectra of both the (N-H) band (L.H.S) and the (O-H) band (R.H.S) in the solvent mixture 15% methyl iodide + 85% n-hexane, at different higher temperature.

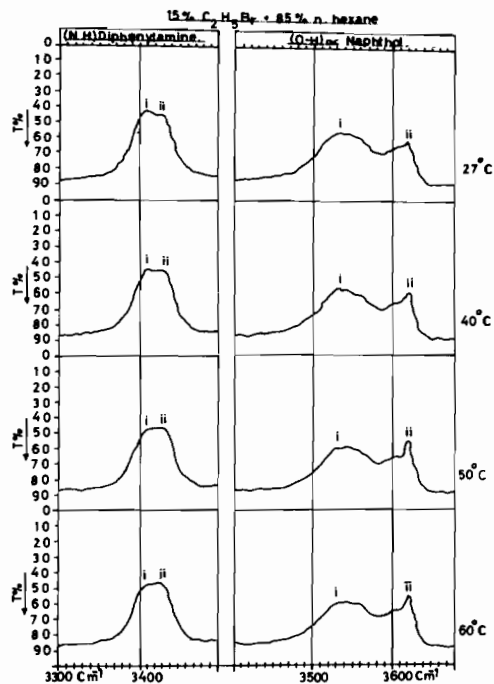


Fig. 9. IR- spectra- both the (N-H) band (L.H.S) and the (O-H) band (R.H.S) in the solvent-mixture 15% ethyl bromide + 85% n. hexane at different higher temperatures.

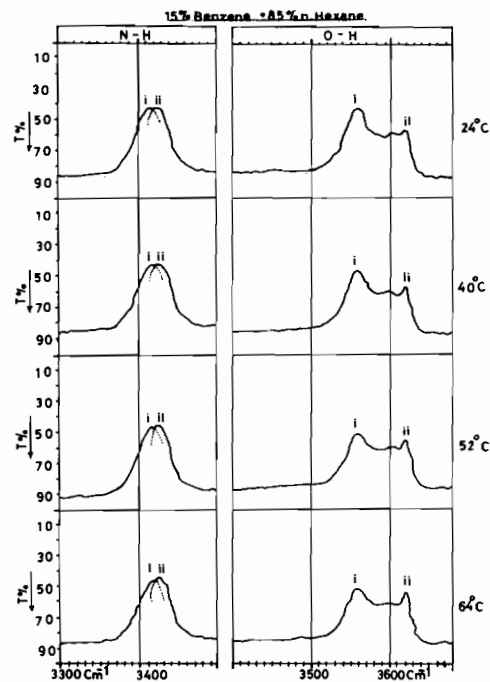


Fig. 10. IR- spectra of both the (N-H) band (L.H.S) and the (O-H) band (R.H.S) in the solvent mixture 15% benzene + 85% n. hexane at different higher temperatures.

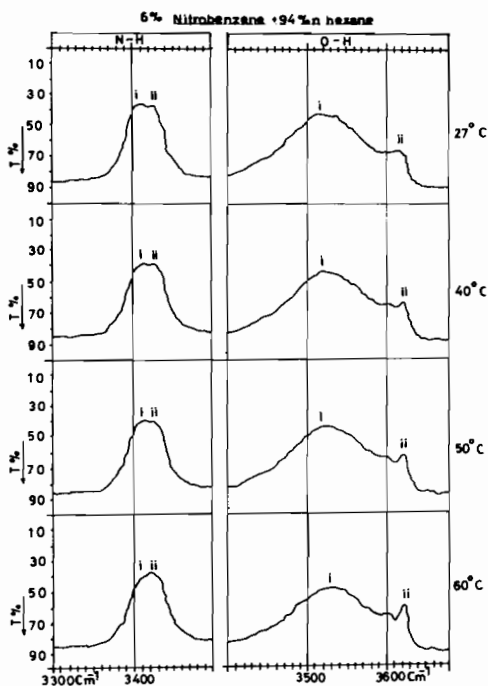


Fig. 11. IR- spectra of both the (N-H) band (L.H.S) and the (O-H) band (R.H.S) in the solvent mixture 6% nitrobenzene + 94% n. hexane at different higher temperature

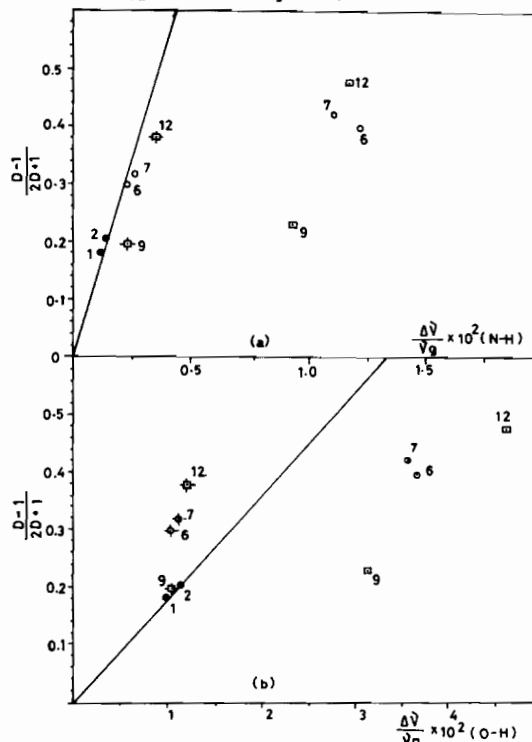


Fig. 12. Relation of $\frac{D-1}{2D+1}$ for the different solvent mixtures against $\frac{\Delta v}{v_g} \times 10^2$ of band (ii) crossed points) for both the (N-H) and the (O-H) bonds compared with the KEM- lines

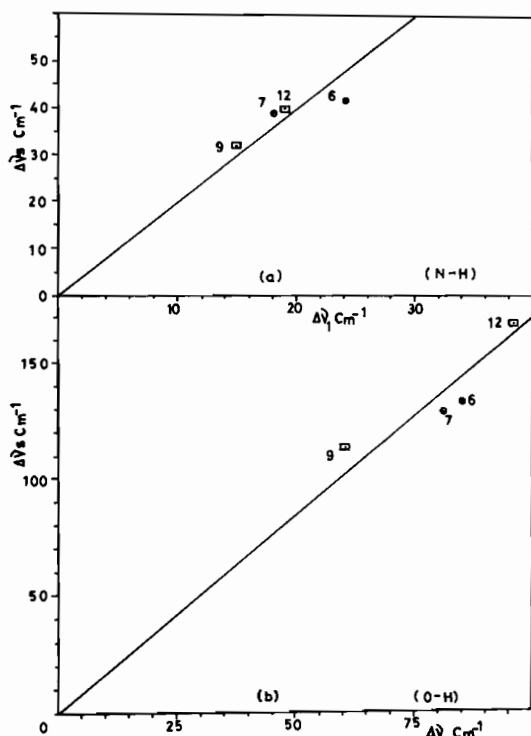


Fig. 13. Relation of the total frequency shifts ($\Delta\bar{\nu}_s$) Cm^{-1} against the frequency shifts ($\Delta\bar{\nu}_i$) Cm^{-1} due to interaction

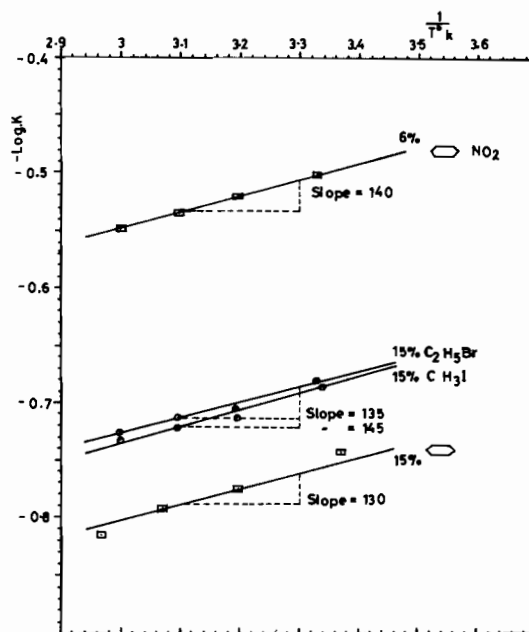


Fig. 14. Relation of $\text{Log} K$ due to the different polar and aromatic solvent components against $\frac{1}{T^{\circ}K}$ for the (N-H) bond

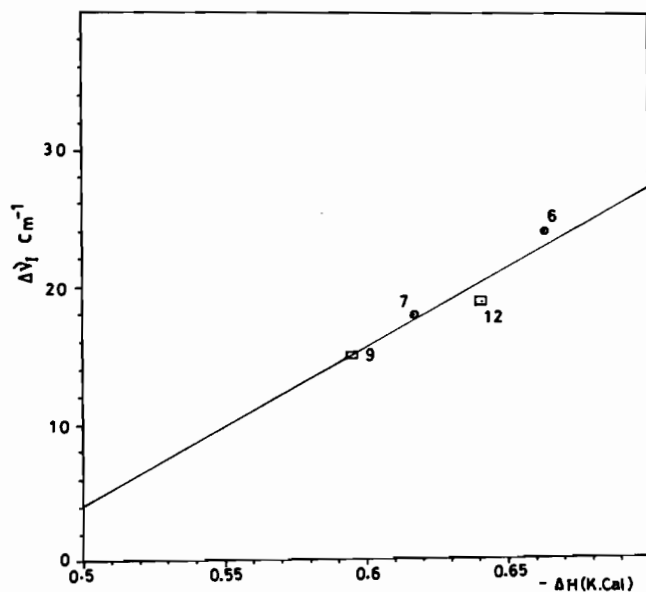


Fig. 15. Relation of the frequency shifts due to interactions ($\Delta\bar{\nu}_i$) Cm^{-1} against heat contents ($-\Delta H$) (K.Cal/model) for the (N-H) bond in the different solvent mixtures

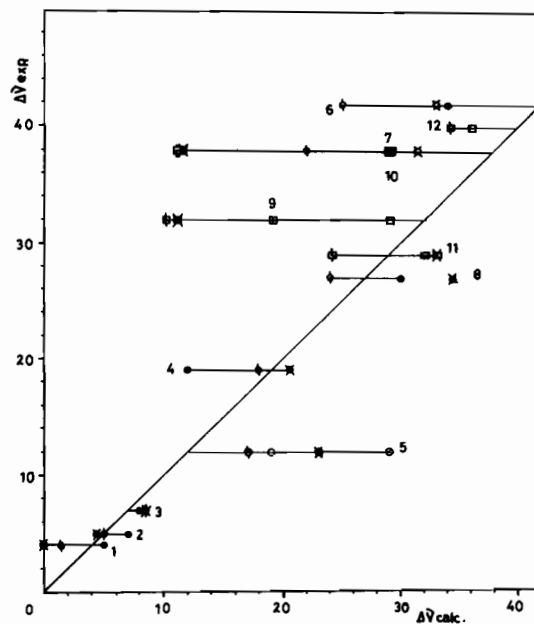


Fig. 16. Relation between $\Delta\bar{\nu}_{\text{exp}}$ and $\Delta\bar{\nu}_{\text{calc}}$, for (N-H)

○ ● refer to $\Delta\bar{\nu}_{\text{calc}}$ by Buckingham's eq. 2,
 ◆ ◆ refer to $\Delta\bar{\nu}_{\text{calc}}$ by McRae
 × × refer to $\Delta\bar{\nu}_{\text{calc}}$ by David & Hallam's . .

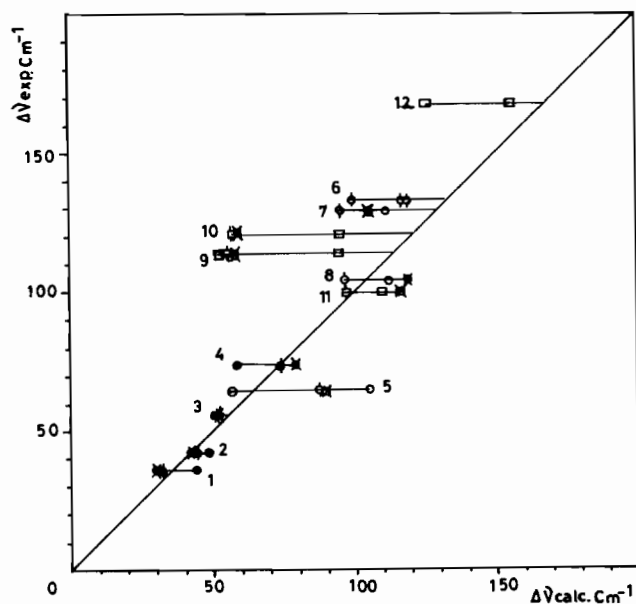


Fig. 17. Relation between $\Delta\nu_{\text{exp}}$ and $\Delta\nu_{\text{calc}}$ for O-H bond

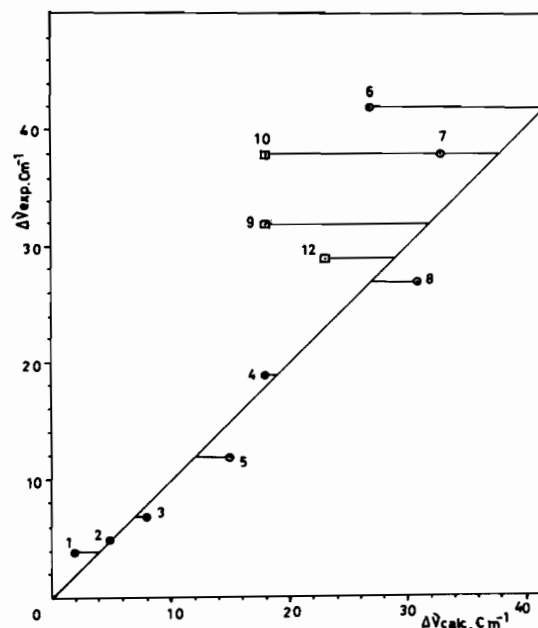


Fig. 18. Relation between $\Delta\nu_{\text{exp}}$ against $\Delta\nu_{\text{calc}}$, cm^{-1} resulting from the authors' equation for the (N-H) bond

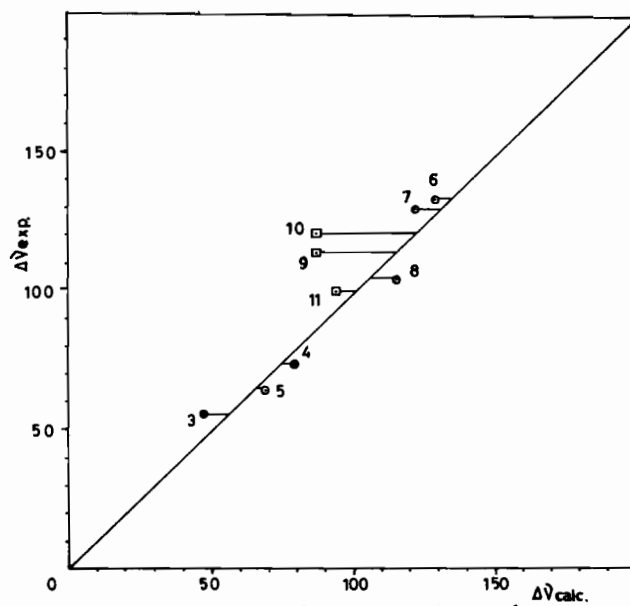


Fig. 19. Relation between $\Delta\nu_{\text{exp}}$ against $\Delta\nu_{\text{calc}}$, cm^{-1} resulting from the authors' equation, for the (O-H) bond

دراسة طيفية لتأثير الوسط على تردد الاشعة دون الحمراء

محمد ابراهيم ناصر وأحمد هاشم بسيوني

قسم الفيزياء بجامعة الكويت وقسم الفيزياء بجامعة الزقازيق

خلاصة

ان تشيع اي مادة يثر فيها ظواهر تكشف عن تركيبها الجزيئي ، وكذلك عن القوى الالكتروستاتيكية الموجودة بين الذرات المركبة لهذه المادة .

وفي هذه الدراسة تم تشيع ثنائي فينل الامين وكذلك الالفنا فتول ، في ثلاث مجموعات مختلفة من المذيبات تمثل انواعا مختلفة للوسط ، وتمت ملاحظة تردد مجموعة الامين (N-H) في المادة الاولى وتردد مجموعة الهيدروكسيل (O-H) في المادة الثانية . ولقد تم قياس تردد المجموعتين المذكورتين في الحالة الغازية لأول مرة عمليا وذلك بعمل خلية حرارية خصيصا لهذا البحث . ولقد أجرى الباحثون السابقون دراساتهم على مواد غازية او سائلة ذات درجات غليان منخفضة مما سهل تحويلها لغازات ، بينما تعرض الباحثان لمادتين صلبتين في حالاتهما العادية ودرجة غليانها المرتفعة مما حدا بهما الى تصميم الخلية المخصوصة المذكورة . وقد بلغت ν_0 للمجموعة الاولى 3636 سم⁻¹ ، وللمجموعة الثانية 3658 سم⁻¹ وهي تفضل كثيرا القيم المستنتجة من المعادلات المختلفة . وبذلك امكن حساب الازاحة في التردد بدرجة تفضل غيرها في الدقة ، وامكن استنتاج بعض الخصائص عن كوامن المواد المذكورة ، منها انه في حالة الوسط غير القطبي فان خواص العزل الكهربائي للمادة تلعب الدور الرئيسي في الازاحة الترددية ، اما في حالة الوسط القطبي فان قوى التفاعل الداخلية بين المسادة والوسط هي التي تلعب الدور الاساسي في الازاحة الترددية .

هذا جزء من دراسة مطولة عن الخاصية التي يراد التوصل الى كنهها وسيتوالى - بمشيئة الله - استقصاؤها .